

Support for R&D to Further Develop Ammonia as a Fuel and Fuel Component

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Prior work has shown that ammonia is a promising transportation fuel and fuel component for internal combustion engines^a and fuel cells^b. More specifically, prior work at Sandia National Laboratories^c has identified the following advantages:

- 1) “It is practical to store energy at much higher density in an ammonia as against a hydrogen-storage system”;
- 2) “Ammonia, like hydrogen, is carbon-free, and ammonia production is a well-established, economical technology (with Haber-Bosch synthesis about 60% energy efficient)”;
- 3) “Closest to realization, for ammonia-fueled transportation, are efficient, clean, internal combustion engines”;
- 4) “In spark-ignition mode, ammonia has high octane (110-130). It has also shown promise in assisted diesel (Army research) and in homogeneous charge compression ignition (HCCI) combustion (van Blarigan, Sandia)”;
- 5) “Alternatively, one can use modest amounts of ammonia as a source for on-board H₂ to improve the efficiency of spark ignition engines”; and
- 6) “Adding small amounts of H₂ to a lean gasoline-air mixture extends the flammability limit of the mixture. This allows higher compression ratios (higher efficiency), colder combustion temperatures (lower NO_x production), and lower throttle losses (higher efficiency; Hydrogen-Enhanced Combustion Engine).”

But the Sandia reference also states that ammonia as a transportation fuel has been limited by several factors. One factor is “that ammonia cracking units capable of supplying the ultra-pure hydrogen needed by PEM fuel cells are too bulky, too heavy and run at too high temperature.”^d Another “important, indeed unavoidable, area of research is on how to make the use of NH₃ acceptably safe without giving up too much of its advantage as a high energy density material.”^e

However, both of these negative factors have been addressed and largely overcome. It is true that PEM fuel cells, which are the DOE and industry choice, certainly do need pure H₂. For H₂ produced by reforming of NH₃, clean-up of any residual NH₃ in the H₂ to negligible levels is not a significant technical challenge. And, if reforming is problematic, pure H₂ can be delivered by electrolysis.^f And it is now also true that NH₃ can be delivered directly to an ammonia fuel cell (non-PEM) as described in many of the references in end note “b” below. And although the NH₃ safety challenge has not been fully overcome for 100% ammonia storage, it’s not as bad as some folks would believe.^g

A new method of storing initially small amounts of ammonia has also been able to fully overcome the major “indeed unavoidable,” safety issues by dissolving ammonia in hydrocarbon fuel mixtures. Specifically, initial ammonia concentrations would be under 1% in hydrocarbon-based fuels for vehicles powered primarily by internal combustion (IC) engines, either gasoline (spark ignition) or diesel (compression ignition) engines. This avoids separate, pressurized ammonia tanks, replacing them with ammonia dissolved primarily in ethanol-diesel and ethanol-gasoline mixtures in concentrations substantially less than the 5-10% ammonia concentrations in common window and household cleaners.^h Safety has also been shown by the following:

- Ammonia is substantially soluble in alcohols including ethanol;^{i j k l}

- Public and proprietary SY-Will Engineering data shows ammonia soluble in several hydrocarbon fuels using an alcohol-based co-solvent package;^{m n o}
- Animal studies have shown limited effects of ammonia at concentrations under 1%;^p
- OSHA Standard for ammonia in the workplace is 50 ppm,^q generally more than the concentration range where ammonia odors are detectable;^r and
- 17.5% ammonia (dissolved in ethyl alcohol) is used as a medical inhalant.^s

In stark contrast to on-board liquid or gaseous hydrogen storage, dissolving small amounts of ammonia in hydrocarbon-alcohol fuels eliminates the safety hazards inherent in the separate on-board pressurized ammonia contained within tanks and piping systems. Dissolving small amount of ammonia also eliminates the inherent safety hazards in the separate storage and handling of pressurized ammonia or hydrogen in the fuel distribution and refilling infrastructures^t.

In addition to making small concentrations of ammonia safe and gaining **ALL** of the above-quoted advantages documented by Sandia National Laboratories, adding ammonia to diesel-ethanol or gasoline-ethanol fuel mixtures allows still further advantages. These include:

- Even lower NOx emissions since a portion of the ammonia-component can be easily stripped off and injected into the exhaust gases to dramatically reduce NOx emissions;^{u v w}
- No new exhaust emissions since ammonia is already a component of IC engine exhausts;^x
- Small evaporative ammonia emissions can be controlled by existing on-board and/or other existing evaporative emission controls;^y and
- In addition to the ethanol component, ammonia can also be derived from coal or renewable stocks.^z

In summary, on-board ammonia cracking units and safety concerns with separate on-board ammonia storage are no longer the stumbling blocks to the further development of ammonia and/or ammonia component fuels. Fuel cells that directly use ammonia have been proven and PEM hydrogen fuel cells can be supplied, if necessary, by hydrogen produced by electrolysis. Safe handling and storage of ammonia has been shown in Farm Belt with 15-20 million tons of NH₃ delivered annually with an outstanding safety record. In addition, a safe record in vehicles has been shown during WW2 in Belgium.^{aa}

Even more so, the major “unavoidable” safety issues have been shown to be **FULLY** avoided for small ammonia concentrations dissolved in hydrocarbon fuel mixtures for vehicles powered by IC engines. These fuel mixtures not only eliminate the separate ammonia on-board and distribution storage and handling risks, but provide added benefits, such as improving fuel economy and drastically reducing NOx emissions, e.g., to meet CARB’s 2010 NOx regulations for heavy duty trucks. Initially dissolving small concentrations of ammonia in hydrocarbon fuel mixtures for existing vehicles provides substantial immediate and cost-effective benefits while also serving as a transition to higher concentrations of ammonia in hydrocarbon fuel mixtures and finally to fuel cell vehicles directly powered by 100% ammonia.

ENDNOTES

^a MacKenzie and J.J. Avery, "Ammonia fuel: the key to hydrogen-based transportation," W.H. World Resources Inst., Washington, DC; Energy Conversion Engineering Conference, 1996. IECEC 96. Proceedings of the 31st Intersociety, Publication Date: 11-16 Aug 1996 Volume: 3, on page(s): 1761-1766 vol.3, at http://ieeexplore.ieee.org/xpl/freeabs_all.jsp?arnumber=553368. See also Hodgson (in PDF format that can be separately transmitted, if required), Hodgson and Graves (separately transmitted in PDF format on CD), Arora and Gupta (in PDF format that can be separately transmitted if required), Steele (separately transmitted in PDF format on CD), Feibelman, "Thoughts on Starting the Hydrogen Economy," Letter to Physics Today, June 2005, page 13, at <http://www.physicstoday.org/vol-58/iss-6/p13.html>, Agosta, "The Ammonia Economy," Web Exclusive, 7/10/03, Mechanical Engineering Magazine, at <http://www.memagazine.org/contents/current/webonly/webex710.html>, George Thomas and George Parks, "Potential Roles of Ammonia in a Hydrogen Economy," US Dept of Energy, Feb 2006, at http://www.hydrogen.energy.gov/pdfs/nh3_paper.pdf, Ted Hollinger, "Performance of a Commercial Internal Combustion Engine on Ammonia Fuel," Hydrogen Energy Center, Inc. 2006 Ammonia Conference, 10/10/06 at <http://www.energy.iastate.edu/Renewable/ammonia/ammonia/2006/HydrogenEngineCenter.pdf>, and "Welcome to the NH₃ Car," Ammonia-Gasoline Powered Vehicle, at <http://nh3car.com/>

^b Kuppinger, Robert E., "Direct Ammonia-Air Fuel Cell," Rept. no. 4 (Final), 1 Jul 63-31 Aug 64, Electrochimica Corp., Menlo Park CA, See also Wynveen (separately transmitted in PDF format on CD), Miller (separately transmitted in PDF format on CD), Vajo, "Ammonia Fuel Cell," US Patent No. 7,157,166 1/2/2007 at <http://www.freepatentsonline.com/7157166.html>, and Jason C. Ganley et al., "An Intermediate Temperature Fuel Cell," Iowa Energy Center, 2007 Ammonia Conference, 10/15/2007, at http://www.energy.iastate.edu/Renewable/ammonia/ammonia/2007/DAFC_Oct2007_Final.pdf

^c Peter J. Feibelman¹ and Roland Stumpf, "Comments on Potential Roles of Ammonia in a Hydrogen Economy – A Study of Issues Related to the Use of Ammonia for On-Board Vehicular Hydrogen Storage," Sandia National Laboratories, at http://www.sandia.gov/surface_science/pjf/On_NH3_roles_in_H2_economy.pdf. See also Thomas and Parks, DOE, cited above in endnote a.

^d Ibid

^e Ibid

^f Vitse, Cooper, and Botte, "On the Use of Ammonia Electrolysis for Hydrogen Production," Journal of Power Sources, 142 (2005) 18-26, at <http://webche.ent.ohiou.edu/eerl/documents/vitse-cooper-botte%20JPS-2005-Ammonia.pdf>

^g Nijs Jan Duijm, Frank Markert, Jette Lundtang Paulsen, "Safety Assessment of Ammonia as a Transport Fuel," RISO National Laboratory, Denmark, February 2005, at <http://www.risoe.dk/rispubl/SYS/syspdf/ris-r-1504.pdf> and footnote aa

^h "Solutions of ammonia (5–10% by weight) are used as household cleaners, particularly for glass," in "Ammonia," Wikipedia, see <http://en.wikipedia.org/wiki/Ammonia>

ⁱ M. J. Clugston and Rosalind Flemming "Advanced Chemistry," Oxford Press, 2000, Chapter 24.2, page 438, section labeled "Ammonia as a Nucleophile," second paragraph, "... usually heated with an excess of ammonia dissolved in ethanol" at <http://books.google.com/books?id=qciCdSFpFPkC&pg=PA438&lpg=PA438&dq=ammonia+%22dissolved+in+ethanol%22&source=web&ots=vK8YnqDVeK&sig=RWYYrWv7FLpQeZCpP8G0ICJ3k>

^j US Patent No. 3,890,339, at <http://patft.uspto.gov/netacgi/nph-Parser?Sect1=PTO1&Sect2=HITOFF&d=PALL&p=1&u=%2Fnethtml%2FPTO%2Fsrchnum.htm&r=1&f=G&l=50&s1=3890339.PN.&OS=PN/3890339&RS=PN/3890339>

^k US Patent No. 6,613,904, at <http://patft.uspto.gov/netacgi/nph-Parser?Sect1=PTO1&Sect2=HITOFF&d=PALL&p=1&u=%2Fnethtml%2FPTO%2Fsrchnum.htm&r=1&f=G&l=50&s1=6613904.PN.&OS=PN/6613904&RS=PN/6613904>

^l “Table V, Solubility of Ammonia in Alcohols,” Airgas Specialty Products, see <http://www.airgasspecialtyproducts.com/UserFiles/laroche/PDF/ATDM-V.pdf>

^m US Patent No. 4,166,724, at <http://patft.uspto.gov/netacgi/nph-Parser?Sect1=PTO1&Sect2=HITOFF&d=PALL&p=1&u=%2Fnethtml%2FPTO%2Fsrchnum.htm&r=1&f=G&l=50&s1=4166724.PN.&OS=PN/4166724&RS=PN/4166724>

ⁿ US Patent No. 1,689,885, at <http://patft.uspto.gov/netacgi/nph-Parser?Sect1=PTO1&Sect2=HITOFF&d=PALL&p=1&u=%2Fnethtml%2FPTO%2Fsrchnum.htm&r=1&f=G&l=50&s1=1589885.PN.&OS=PN/1589885&RS=PN/1589885>

^o European Patent No. EP 1,246,889, at <http://patft.uspto.gov/netacgi/nph-Parser?Sect1=PTO1&Sect2=HITOFF&d=PALL&p=1&u=%2Fnethtml%2FPTO%2Fsrchnum.htm&r=1&f=G&l=50&s1=1589885.PN.&OS=PN/1589885&RS=PN/1589885>

^p S. S. S. Sarma, Ernesto Mangas-Ramírez, and S. Nandini, “Effect of Ammonia Toxicity on the Competition Among Three Species of Cladocerans,” in *Ecotoxicology and Environmental Safety*, June 2003, Pages 227-235, at <http://www.custom-kits.com/MSDS/Amm%20Inh.pdf>

^q “Ammonia in Workplace Environments,” US Department of Labor Occupational Safety & Health Administration, at <http://www.osha.gov/dts/sltc/methods/partial/id164/id164.html>

^r “Anhydrous Ammonia Safety Information,” Dakota Gasification Company, at http://www.dakotagas.com/Products/Safety%20Information/Anhydrous_Ammonia_Sa.html

^s “Ammonia Inhalant Material Safety Data Sheets (MSDS),” James Alexander Corp., at <http://www.custom-kits.com/MSDS/Amm%20Inh.pdf>

^t “Ammonia Spills in New York State 1993-1998 Hazardous Substances Emergency Events Surveillance Project,” State of New York Department of Health, at <http://www.health.state.ny.us/environmental/chemicals/hsees/ammonia.htm>

^u US Patent 3,900,554, at <http://patft.uspto.gov/netacgi/nph-Parser?Sect1=PTO1&Sect2=HITOFF&d=PALL&p=1&u=%2Fnethtml%2FPTO%2Fsrchnum.htm&r=1&f=G&l=50&s1=3900554.PN.&OS=PN/3900554&RS=PN/3900554>

^v US Patent No. 5,224,346, at <http://patft.uspto.gov/netacgi/nph-Parser?Sect1=PTO1&Sect2=HITOFF&d=PALL&p=1&u=%2Fnethtml%2FPTO%2Fsrchnum.htm&r=1&f=G&l=50&s1=5224346.PN.&OS=PN/5224346&RS=PN/5224346>

^w US Patent No. 5,609,026, at <http://patft.uspto.gov/netacgi/nph-Parser?Sect1=PTO1&Sect2=HITOFF&d=PALL&p=1&u=%2Fnetahml%2FPTO%2Fsrchnum.htm&r=1&f=G&l=50&s1=5609026.PN.&OS=PN/5609026&RS=PN/5609026>

^x A typical car emits 0.28 ounces of ammonia per hundred miles, “Catalytic Converters Fix One Pollution Problem, Cause Another,” CNN, Nov 27, 2000, at <http://edition.cnn.com/2000/NATURE/11/27/cataytic.converters.enn>

^y Chun Yi Liu and Ken-Ichi Aika, “Modification of active carbon and zeolite as ammonia separation materials for a new de-NO_x process with ammonia on-site synthesis,” Research on Chemical Intermediates, Volume 28, No. 5 / July, 2002 at <http://www.springerlink.com/content/3pategagmwyrvrgj/>

^z Bill Leighty, Leighty Foundation, “Costs of Delivered Energy from Large-scale, Diverse, Stranded, Renewable Resources, Transmitted and Firmed as Electricity, Gaseous Hydrogen, and Ammonia” Ammonia - The Key to US Energy Independence, Oct 9-10, 2006, Denver, at <http://www.energy.iastate.edu/Renewable/ammonia/ammonia/ammoniaMtg06.htm>

^{aa} Hodgson experience, at <http://nh3car.com/>, and safe storage approaches at <http://www.energy.iastate.edu/Renewable/ammonia/ammonia/2006/AnalyticPowerCorp.pdf>